Recursive approach to copolymerization statistics

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A new method is presented for calculating average values of molecular weight, chain length and sequence distributions in linear copolymerization. The method provides a considerable expedient to these results over most other approaches since the average values are calculated directly, bypassing the calculation of distributions themselves. The approach is applicable to polymerizations possessing a first order Markovian statistical character, and relies on the recursive nature of this type of chain. Several examples are given, some new results for the AA, BB, CC (urethane-like) system are obtained and the recursive approach is contrasted with older approaches.

INTRODUCTION

Many alternative approaches may be taken in deriving expressions for molecular weight, molecular weight (or chain length) distribution (*MWD* or *CLD*) and sequence lengths resulting from simple polymerization mechanisms[1,2]. The approaches may be grouped into two broad categories. There are deterministic approaches, which start with the differential equations for the time rates of change of the various species in the reacting system. These types of approaches necessarily involve the solution of an infinite set of differential equations to give the molecular weight distribution. Special techniques can accomplish this analytically in some cases. When possible, this gives the solution for the full time development of the *MWD*. The other category is that of statistical approaches, which make use of probabilistic arguments. These approaches almost always, either explicitly or implicitly, model the polymerization as a first-order Markov chain process. For simple mechanisms the chain length distribution can often be written down directly, since there are few, or perhaps only one, elements in the transition probability matrix. Intuition serves well in these simple cases. However, in cases of multicomponent polymerization, or other complicating factors in the polymerization mechanism, intuition may fall short. A formal machinery can be set up to handle these more complex cases, as we shall see, either in terms of a direct summation approach[3] or the more elegant formalism of Markov chain theory[4,5]. A disadvantage of all probabilistic approaches, although not too severe, is that the results for *MWD* and *CLD* are always developed in terms of some (one or more) probability which must be associated with a parameter of the reaction, such as a fractional conversion of some reacting group. A model for the time evolution of the *MWD* must result from an independent model of this conversion vs. time. A little-exploited advantage of some statistical methods is that they sometimes reveal some interesting stochastic character of the polymerization[4,5]. The expressions for some interesting multicomponent polymerizations are both unwieldy and difficult to generate using the formal mechanisms.

We are interested in a class of polymerizations which are difficult to model by any of the available approaches. These are linear step-growth copolymerizations where temperature varies both spatially and temporally in the polymerizing medium, where unequal reactivity may be important, and a phase separation may take place during the reaction. Urethane polymerization under conditions appropriate to the reaction injection-moulding process is a prime example of a practical process showing these complexities[6]. There are also indications that certain copolyamidations may be subject at least to the latter phenomenon[7]. Because of our interest in the reaction injection moulding process and the complexities attendant to applying any of the formal machineries to the task of calculating *MWD, CLD* and sequence distributions, we have developed, and present in this paper, a new conceptual approach to the calculation of the *average* properties of these distributions. It is a probabilistic approach and therefore the resulting equations must be augmented with a set of kinetic differential equations to reveal the behaviour with time. However, the merit of the approach presented here is that it obtains the average values of the distributions directly, to give rather simple expressions even in the face of unequal reactivities and other complexities which severely obstruct the more formal and complete methods.

The method to be described here utilizes the recursive nature of the linear Markov chain process. It is identical in concept to a new method recently presented by Macosko and Miller for calculating molecular weight averages for nonlinear polymers[8]. Results for certain linear polymerizations can be deduced directly from their equations. Our purpose here is to highlight these aspects and to work through some examples of important multicomponent linear copolymerizations. The method uses the so-called law of total probability of expectation, which may be stated in the following way. Let A be an event, $\bar{A}$ its complement. Let Y be a random variable, $E(Y)$ its expectation (or average value), and

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$E(Y/A)$ its conditional expectation, given that the event A has occurred. $P(A)$ is the probability that event A occurs. Then the law of total probability for expectation is:

$$E(Y) = E(Y/A)P(A) + E(Y/\bar{A})P(\bar{A}) \qquad (1)$$

This law is discussed in most introductory books on probability theory[9].

The goals of this work are to develop this new method as a tool for calculating molecular weight averages in linear multicomponent copolymerizations, which is useful and straightforward to use even when the mechanisms are complex or temperature is an important variable, to calculate average values of the sequence distribution from the same unified approach, and to compare and contrast with previous approaches, where possible, to highlight advantages and disadvantages of each. A brief review of other approaches is thus in order before describing the recursive approach. Most of the discussion here will be presented in terms of step-growth polymerization, although with proper identification of the transition probabilities most of the statistical developments are equally applicable to chain-growth polymerization.

BACKGROUND ON OTHER APPROACHES

Flory[10] recognized the Markov chain nature of most polymerization processes and showed how, for the simplest mechanisms, consideration of the reaction (transition) probabilities leads to a geometric distribution of molecular weights and chain lengths. For a linear polycondensation of an AB-type monomer, we need only ask for the probability, P_x, of forming a macromolecule of x units by adding exactly $(x - 1)$AB units to an original AB unit and then no further additions are made. This may be written down directly as

$$P_x = p^{x-1}(1 - p) \qquad (2)$$

where p is the probability of reaction having occurred for any A (or B) group chosen at random, that is, the fractional conversion of A or B end-groups*. Since

$$\sum_{x=1}^{\infty} P_x = 1$$

we can identify the P_x with the mole fractions N_x of polymer molecules of length x, and the geometrical nature of the number chain length distribution is clear. Other well-known results for this reaction system are those for the distribution of numbers of polymers, η_x, of length x:

$$\eta_x = N_0 p^{x-1}(1 - p)^2 \qquad (3)$$

where N_0 is the initial number of AB units present; the number-average chain length:

$$\bar{x}_n = \frac{1}{1 - p} \qquad (4)$$

and the weight-average chain length:

$$\bar{x}_w = \frac{1 + p}{1 - p} \qquad (5)$$

For more complicated cases of interest, Case[3] has demonstrated how the above principles may be applied in a conceptually straightforward way to give the number chain length (*CLD*) and molecular weight (*MWD*) distributions. Consider briefly now the case of AA, BB, CC step-growth copolymerization, adopting Case's notation, (where BB and CC do not react with one another), a case of importance to commercial urethane polymerization to be considered in more detail in a later section. Six types of polymer molecules, classified by their two end-groups, exist (AA, BB, CC, AB, AC, BC). *Each* will have a geometrical distribution of chain lengths which may be written down directly following the same line of reasoning which leads to equation (2). The overall *MWD* or *CLD* is the sum of the individual distributions, weighted by their respective mole fractions. The resulting expressions are quite unwieldy, and extremely difficult to use to calculate moments and average molecular weights. For this reason, expressions for some of the experimentally accessible average molecular weights have never been published even though Case's work[3] is more than twenty years old. Another disadvantage of this approach is that analysis of sequence distributions requires a parallel and equally unwieldy development.

When it is not possible or straightforward to derive the desired expression from direct mechanistic reasoning, Lowry[4] has shown how it is possible to combine the various probabilities of reaction in a Markov-chain transition matrix and then obtain the *CLD* and its moments by matrix manipulation. Since one is interested in chains of finite length, termination ('absorption') probabilities are included in the transition probability matrix, thus we are dealing with 'absorbing' Markov chains. For this type of problem, the transition probability matrix $\underline{\underline{P}}$ can be partitioned into submatrices in the following way:

$$\underline{\underline{P}} = \begin{pmatrix} \underline{\underline{I}} & \underline{\underline{O}} \\ \underline{\underline{R}} & \underline{\underline{Q}} \end{pmatrix} \qquad (5)$$

The rank of the square matrix $\underline{\underline{P}}$ is one greater than the number of transient states in the Markov-chain process which represents the polymerization. For analysing step-growth polymerizations the most convenient approach is to envision a sequential counting process on already-formed chains, at some extent of reaction, as being the Markovian process. A particular transient state is then identified as the presence of a particular comonomer unit at some position along the chain, and the transition probabilities between the transient states are the probabilities that some one of the other states (comonomers) follows the 'present' state along the chain. If reaction (transition) between a particular pair of monomers (transient states) is forbidden, a zero transition probability results. Thus, there are as many transient states as there are comonomers in the reaction, let us say N. In Equation (5), $\underline{\underline{Q}}$ is an $N \times N$ matrix of probabilities of transition among

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* The probability would have a different interpretation for an addition polymerization mechanism. In that case p would be the instantaneous probability that a propagation step occurs, with respect to all the alternatives. Lowry[4] gives a more complete discussion of how, and the extent to which, much of what is discussed here for step-growth polymerization also applies to chain-growth polymerization

the various transient states. $\underline{\underline{R}}$ is an $N \times 1$ matrix† of probabilities of absorption (termination) from each of the transient states. Termination or absorption in this process is the state of having *no* comonomer unit following the 'present' state. $\underline{\underline{O}}$ is a $1 \times N$ matrix† containing only zeros which indicates the impossibility of a transient state being reached from an absorbing state. In this case, where we have only one absorbing state (termination or, actually, the state of having *no* comonomer unit following the 'present' state),† $\underline{\underline{I}} = 1$ which assures that once the system enters the absorbed state (terminates), it stays there. The $\underline{\underline{P}}$ matrix is stochastic. This sequential counting process must begin at a chain end if it is to count all the units and give us the *CLD* and so, besides knowledge of the elements of $\underline{\underline{P}}$, we need to know $\mathbf{q}^o$, the vector of probabilities of each of the transient states (comonomer units) initiating (occurring at the end of) a chain. With these two arrays of information, Lowry shows, using the stochastic quality of $\underline{\underline{P}}$, that the *CLD* is given by:

$$P_x = \mathbf{q}^o \underline{\underline{Q}}^{x-1}(\underline{\underline{I}} - \underline{\underline{Q}})\mathbf{1} \qquad (6)$$

where $\underline{\underline{I}}$ is the identity matrix of rank N and $\mathbf{1}$ is an N-dimensional column vector of ones. Any moment of P_x, λ_r, may be calculated from:

$$\lambda_r = \mathbf{q}^o \mathbf{t}_r \qquad (7)$$

where the $\mathbf{t}_r$ are given by the following recursion formula:

$$\mathbf{t}_r = \mathbf{t}_1 + [(\underline{\underline{I}} - \underline{\underline{Q}})^{-1} - \underline{\underline{I}}] \sum_{k=1}^{r-1} \binom{r}{k} \mathbf{t}_k \qquad (8)$$

$$\mathbf{t}_1 = (\underline{\underline{I}} - \underline{\underline{Q}})^{-1}\mathbf{1} \qquad (9)$$

In particular, this leads to:

$$\bar{x}_n = \lambda_1 = \mathbf{q}^o(\underline{\underline{I}} - \underline{\underline{Q}})^{-1}\mathbf{1} \qquad (10)$$

$$\bar{x}_w = \frac{\lambda_2}{\lambda_1} = \frac{\mathbf{q}^o[2(\underline{\underline{I}} - \underline{\underline{Q}})^{-1} - \underline{\underline{I}}](\underline{\underline{I}} - \underline{\underline{Q}})^{-1}\mathbf{1}}{\mathbf{q}^o(\underline{\underline{I}} - \underline{\underline{Q}})^{-1}\mathbf{1}} \qquad (11)$$

Notice that equation (6) is simply a matrix generalization of equation (2). For the case of AB polymerization, we have $\underline{\underline{Q}} = (p)$ and $\mathbf{q}^o = 1$, thus $(\underline{\underline{I}} - \underline{\underline{Q}})^{-1} = 1/(1-p)$ and by application of equations (6), (10) and (11) the results of equations (2), (4) and (5) are recovered. For more complicated cases, we diagonalize $\underline{\underline{Q}}$ by a similarity transformation and evaluate $\underline{\underline{Q}}^{x-1}$ from:

$$\underline{\underline{Q}}^{x-1} = \underline{\underline{S}}^{-1}\underline{\underline{E}}^{x-1}\underline{\underline{S}} \qquad (12)$$

where $\underline{\underline{E}}^{x-1}$ is the matrix which has the eigenvalues of $\underline{\underline{Q}}$ raised to the $x-1$ (e_i^{x-1}) along the principal diagonal, and $\underline{\underline{S}}$ is the matrix of eigenvectors $\mathbf{a}_i$ corresponding to the e_i. While the matrix manipulations generate compact matrix formulae, it is very tedious to develop the corresponding algebraic formulae, especially for P_x. Of course, we can perform the matrix computations numerically on the computer. This is the prime advantage of the Markov chain formalism over Case's direct summation technique. One serious disadvantage of this approach is that there is no obvious way of putting the molecular weights of the individual comonomers into this scheme and thus calculate *MWD*, instead of *CLD*, and their respective averages. This is a problem with copolymerizations since it is often molecular weight, and not total number of units incorporated into a chain, which is experimentally accessible or desired.

Peller[11] has presented an approach which is very similar in concept to the Markov chain approach described above. He works in terms of a matrix $\underline{\underline{M}}$, of 'sequential' probabilities which are different from, but related to, the Markov chain transition probabilities. Through matrix manipulations akin to those used in the treatment of the statistical thermodynamics of one-dimensional systems, he shows that for the system A_1–B_1 copolymerizing with A_2–B_2 (representative of two different hydroxy- or amino-acids) the *CLD* may be calculated from:

$$P_x = (1\ \ 1)\underline{\underline{M}}^{x-1}\begin{pmatrix} P^1 \\ P^2 \end{pmatrix} \qquad (13)$$

where P^1 and P^2 are the mole fractions of monomers 1 and 2 respectively.

$$\underline{\underline{M}} = \begin{pmatrix} P_{11} & P_{12} \\ P_{21} & P_{22} \end{pmatrix}$$

the matrix of sequential probabilities, that is, P_{ij} is the probability of monomer j following monomer i along the chain. The first two moments of P_x are obtained by differentiation of $\underline{\underline{M}}^x$ and given by:

$$\lambda_1 = \bar{x}_n = (1\ \ 1)\left(\sum_{n=1}^{\infty} \frac{d\underline{\underline{M}}^x}{d\underline{\underline{M}}}\right)\begin{pmatrix} P^1 \\ P^2 \end{pmatrix} \qquad (14)$$

and

$$\lambda_2 = \lambda_1 \bar{x}_w = (1\ \ 1)\left(\sum_{n=1}^{\infty} \underline{\underline{M}}\frac{d^2\underline{\underline{M}}^x}{d\underline{\underline{M}}^2} + \sum_{n=1}^{\infty}\frac{d\underline{\underline{M}}^x}{d\underline{\underline{M}}}\right)\begin{pmatrix} P^1 \\ P^2 \end{pmatrix} \qquad (15)$$

For the case of a single AB monomer, the two dimensional quality of the above matrices and vectors collapses to one and we have $\underline{\underline{M}} = (p)$ and $P^1 = 1 - p$ and by application of equations (13), (14) and (15) the results of equations (2), (4) and (5) are recovered. This method, while having the same usefulness and elegance of the Markov chain approach, also has the same drawbacks. Primary among these are: (1) the lack of a clear way to incorporate monomer molecular weights to be able to calculate *MWD* instead of *CLD* and (2) the extreme unwieldiness of the formal machinery in generating useful algebraic expressions for average degrees of polymerization for even moderately elaborate reaction schemes. Peller does extend his treatment to give a unified analysis of sequence distribution as well and that is an advantage.

Deterministic approaches to these problems are of course also possible[12]. However, no analytical results can usually be obtained for *MWD* or *CLD* from the systems of differential equations except in the very simplest cases. Peebles[13] has

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† If there is more than one absorbing state (unusual for polymerization models) say n, $\underline{\underline{R}}$ is $N \times n$, $\underline{\underline{O}}$ is $n \times N$ and $\underline{\underline{I}}$ is the $n \times n$ identity matrix

combined the deterministic and statistical approaches in a novel way, in developing a set of differential equations for *number-average sequence length*, $\bar{N}_n$, of BB segments in the AA, BB, CC system mentioned above. The analysis is involved, but does lead to a simple analytical expression in the simple limiting case of equal reactivity, 100% conversion, and exact stoichiometric balance between the sum of B and C groups and A groups. He then uses statistical arguments to demonstrate the geometrical nature of the BB sequence distribution. Sorta and Melis[14] and Frensdorff[15] have also considered the sequence distribution problem independently, under the equal reactivity assumption.

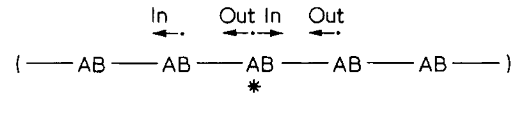
The purpose of the new approach presented here are (1) to avoid some of the cumbersome qualities of formal machineries by calculating the average values of these distributions in a novel way; (2) to develop a statistical approach equally capable of calculating average molecular weights and average degrees of polymerization; and (3) to treat the average properties of *MWD, CLD* and sequence distribution with a unified approach avoiding the necessity of all simplifying assumptions of equal reactivity and stoichiometry.

The method is demonstrated below with three examples, each of which has been treated previously by one of the above methods under certain simplifying assumptions. These will serve to establish the validity and usefulness of the approach, especially in calculating average values of distributions in linear copolymerizations.

RESULTS

Simple AB step-growth homopolymerization

The polymer resulting from the AB homopolymerization is shown below:



Picking an A group at random, we define the 'in' direction from the chosen A toward the B group from the same original monomer unit. 'Out' is then the opposite direction, from the chosen A toward the remainder of the chain on the 'A' side of the monomer. Similar definitions apply to the 'in' and 'out' directions associated with B groups.

We begin by asking for the expected weight of the polymer chain attached to a randomly-chosen A group looking 'out', $E(W_A^{out})$. By application of equation (1) we can express this expected weight in words, as being equal to the expected weight attached to an A looking 'out', conditional on A having reacted with B, *times* the probability of A reacting with B (p) *plus* the expected weight attached to an A looking 'out' conditional on A not having reacted, *times* the probability of A not reacting, $1-p$. Symbolically we write:

$$E(W_A^{out}) = E(W_A^{out}/\text{A reacts } w/\text{B})p + E(W_A^{out}/\text{A does not react } w/\text{B})(1-p) \quad (16)$$

(Throughout the remainder of this paper we will use the abbreviation '*r*' for 'reacts with' and '*dnr*' for 'does not react with'.)

The second term of equation (16) is clearly zero, thus:

$$E(W_A^{out}) = E(W_A^{out}/\text{A}r\cdot\text{B})p \quad (17)$$

The expected weight attached to an A looking 'out' given that that A has reacted with a B must be equal to the expected weight attached to a B group looking 'in':

$$E(W_A^{out}/\text{A}r\cdot\text{B}) = E(W_B^{in}) \quad (18)$$

The expected weight attached to a *B* looking 'in' is equal to the weight of an AB-mer plus the expected weight attached to an A looking 'out':

$$E(W_B^{in}) = M_{AB} + E(W_A^{out}) \quad (19)$$

Equations (17), (18) and (19) are 3 equations with 3 unknowns, which may be solved to give the unknown expected weights. If we begin instead by asking for the expected weight attached to a B group looking out, we arrive at a parallel set of 3 equations by the same arguments:

$$E(W_B^{out}) = E(W_B^{out}/\text{A}r\cdot\text{B})p + \underset{0}{E(W_B^{out}/\text{A}\,dnr\cdot\text{B})}(1-p) \quad (20)$$

$$E(W_B^{out}/\text{A}r\cdot\text{B}) = E(W_A^{in}) \quad (21)$$

$$E(W_A^{in}) = M_{AB} + E(W_B^{out}) \quad (22)$$

The recursive nature of these chains is thus clear. Choosing a starting point somewhere along the chain and moving along the chain in some direction will always eventually result in reaching another position statistically equivalent to the starting point.

Average molecular weights are calculated by recognizing that the weight-average molecular weight will be given by the sum of the weight of an AB mer unit plus the expected weights attached to each arm looking 'out'.

$$\bar{M}_w = M_{AB} + E(W_A^{out}) + E(W_B^{out}) \quad (23)$$

or analogously for weight-average chain length:

$$\bar{x}_w = 1 + E(N_A^{out}) + E(N_B^{out}) \quad (24)$$

where the $E(N)$ are expected *numbers* of units attached. The equations for the $E(N)$ are identical to those for the $E(W)$ except M_{AB} is replaced by 1 wherever it appears. Solving equations (17) to (22) and the analogous equations for the $E(N)$ gives:

$$E(W_A^{out}) + E(W_B^{out}) = M_{AB}\frac{p}{1-p};\quad E(N_A^{out}) = E(N_B^{out}) = \frac{p}{1-p} \quad (25)$$

$$E(W_A^{in}) = E(W_B^{in}) = M_{AB}\frac{p}{1-p};$$

$$E(N_A^{in}) = E(N_B^{in}) = \frac{p}{1-p} \quad (26)$$

Thus, the well known result is obtained by substituting into equations (24) and (25):

$$\bar{M}_w = M_{AB} + M_{AB}\frac{p}{1-p} + M_{AB}\frac{p}{1-p} = M_{AB}\frac{1+p}{1-p} \quad (27)$$

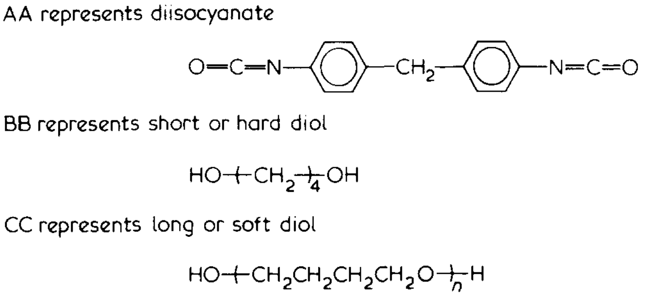


Figure 1 Example of AA, BB, CC system

and

$$\bar{x}_w = \frac{1+p}{1-p}$$

Number-average molecular weights and chain lengths are obtained from the same equations in the following way. In the above calculations, we have picked *mer units* at random; this is a 'weight-averaging' process for molecules; since the larger the molecule, the proportionately larger chance it has of being chosen. If instead we choose *molecules* at random, by picking *chain ends* at random, and ask for the expected weight attached to the end group looking 'in', we obtain a 'number-averaged' quantity. If we pick end-groups, we must statistically weight the $E(W^{\text{in}})$ by the mole fraction of each type of end-group, that is, the mole fractions of unreacted A and B, (x_{A} and x_{B}, in this case); thus:

$$\bar{M}_n = x_{\text{A}} E(W_{\text{A}}^{\text{in}}) + x_{\text{B}} E(W_{\text{B}}^{\text{in}})$$

$$\bar{x}_n = x_{\text{A}} E(N_{\text{A}}^{\text{in}}) + x_{\text{B}} E(N_{\text{B}}^{\text{in}}) \tag{28}$$

Since there are equal numbers of A and B ends in this simple case, $x_{\text{A}} = x_{\text{B}} = ½$, and we get from equations (26) and (28):

$$\bar{M}_n = M_{\text{AB}}(½)\frac{1}{1-p} + M_{\text{AB}}(½)\frac{1}{1-p} = M_{\text{AB}}\frac{1}{1-p}$$

and

$$\bar{x}_n = \frac{1}{1-p} \tag{29}$$

Thus, the well-known results of equations (4) and (5) are recovered.

We have gone into great detail in the calculation for this case, since it is one upon which intuition works well and therefore insight can be obtained into the mechanics and basis of the recursive method.

For simple cases, our approach is no more streamlined than the older approaches. This example does show quite well how the method works. The first order Markovian character is built into our approach on the impliciit assumption that it is only the immediately previous group along the chain which affects the likelihood of a given unit being present on the next step. This will become clearer in subsequent sections, and accounts for the fact that the averages calculated by this method reflect a geometrical quality of the distributions ($\bar{M}_w/\bar{M}_n \to 2$ as $p \to 1$). The direct calculation of *averages* using this method gives considerable streamlining in more complex cases.

AA, BB, CC step-growth copolymerization

An example of this system is the reaction which forms a thermoplastic polyurethane (TPU) elastomer. A typical TPU system consists of a diisocyanate (AA), a short (or 'hard') diol (BB) and a long (or 'soft') diol (CC), as shown schematically in *Figure 1*. The hydroxyl groups of BB and CC react with the isocyanate groups of AA to form the urethane linkage.

It is customary to consider average properties as functions of the extents of reaction, or fractional conversions, of the reactants. For this system we define the following extents of reaction:

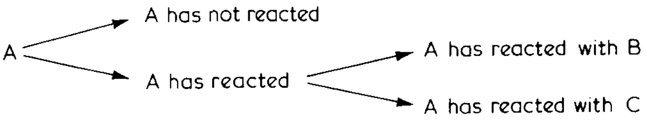
$$p = \frac{A_0 - A}{A_0} \tag{30}$$

$$q_1 = \frac{B_0 - B}{B_0} \tag{31}$$

$$q_2 = \frac{C_0 - C}{C_0} \tag{32}$$

where A, B and C denote concentrations of the various reactive *end-groups* and the subscript zero indicates the values at zero time. We shall derive the various averages in terms of p, q_1 and q_2. In the Appendix we show how to relate them to the polymerization kinetics. We will make the following general assumptions in our treatment: (1) all groups react independently of one another and (2) all reactive groups of the same type (A, B, C) react equally, but we do *not* assume equal reactivity of B and C with A. (Some other manifestations have of unequal reactivity also been treated by Miller and Macosko[16].)

We represent the polymerization of AA, BB and CC schematically in *Figure 2*. This Figure serves to define the various 'directions' in our development of recursion relations. Let this system polymerize to an extent p of the A groups, q_1 of the B groups and q_2 of the C groups. Now, pick an A group at random. What is the weight, $W_{\text{A}}^{\text{out}}$, attached to an A looking out from its parent molecules, in the direction $\xrightarrow{1}$? Since the A is chosen at random, $W_{\text{A}}^{\text{out}}$ is a random variable. A has three possible states:



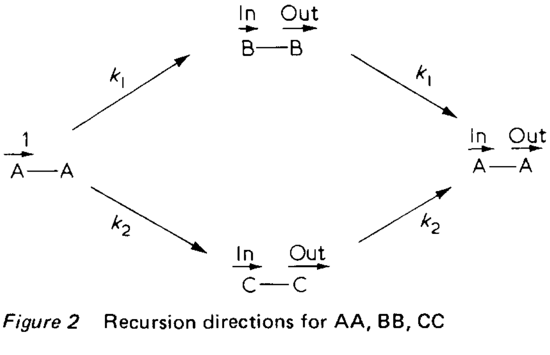


Figure 2 Recursion directions for AA, BB, CC

Thus, W_A^{out} can have any one of three values:

$$W_A^{\text{out}} = \begin{cases} 0 \text{ if A has not reacted} \\ W_B^{\text{in}} \text{ if A has reacted with B} \\ W_C^{\text{in}} \text{ if A has reacted with C} \end{cases}$$

Application of equation (1) gives:

$$E(W_A^{\text{out}}) = E(W_B^{\text{in}})p_{AB} + E(W_C^{\text{in}})p_{AC} + \underbrace{0(1 - p_{AB} - p_{AC})}_{0} \tag{33}$$

where p_{AB} and p_{AC} are the probabilities that A reacts with B and C, respectively. Clearly:

$$p_{AB} + p_{AC} = p \tag{34}$$

In terms of concentrations, we have:

$$p_{AB} = \frac{\text{Moles of B reacted}}{\text{Total moles of B and C reacted}}$$

$$p_{AC} = \frac{\text{Moles of C reacted}}{\text{Total moles of B and C reacted}} \tag{35}$$

Therefore:

$$p_{AB} = \frac{B_0 - B}{B_0 - B + C_0 - C}\,p = \frac{q_1 B_0}{q_1 B_0 + q_2 C_0}\,p \tag{36}$$

$$p_{AC} = \frac{C_0 - C}{B_0 - B + C_0 - C}\,p = \frac{q_2 C_0}{q_1 B_0 + q_2 C_0}\,p \tag{37}$$

The probabilities appearing in these equations are identical to those which would compose a transition probability matrix in the Markov chain approach; they are distinct from the 'sequential' probabilities of Peller[11] in ways which can only be fully appreicated by reading his paper. From stoichiometric arguments it is clear that:

$$A_0 p = B_0 q_1 + C_0 q_2 \tag{38}$$

and therefore

$$p_{AB} = r_1 q_1; \quad p_{AC} = r_2 q_2 \tag{39}$$

where

$$r_1 = B_0/A_0; \quad r_2 = C_0/A_0 \tag{40}$$

The expected weight on any B group looking into its parent molecule, $E(W_B^{\text{in}})$, will be the molecular weight of BB plus the expected weight on the other arm, which is just $E(W_B^{\text{out}})$:

$$E(W_B^{\text{in}}) = M_{BB} + E(W_B^{\text{out}}) \tag{41}$$

Similarly:

$$E(W_C^{\text{in}}) = M_{CC} + E(W_C^{\text{out}}) \tag{42}$$

Following the arrows in *Figure 2* we can continue to write relations for the expected weights until the recursive nature of the structure brings us back to equation (33).

$$E(W_B^{\text{out}}) = E(W_B^{\text{out}}/\mathrm{B}r\cdot\mathrm{A})q_1 + \underbrace{E(W_B^{\text{out}}/\mathrm{B}dnr\cdot\mathrm{A})(1 - q_1)}_{0} \tag{43}$$

Since BB and CC react only with AA:

$$E(W_B^{\text{out}}) = E(W_A^{\text{in}})q_1 \tag{44}$$

$$E(W_C^{\text{out}}) = E(W_A^{\text{in}})q_2 \tag{45}$$

An finally,

$$E(W_A^{\text{in}}) = M_{AA} + E(W_A^{\text{out}}) \tag{46}$$

Equations (33), (41), (42) and (44)–(46) constitute a set of six equations and six unknowns which can be solved for the expected weights. The molecular weight, W_{AA}, of the entire molecule to which a randomly chosen AA belongs will be the molecular weight of AA plus the expected weight attached to both arms:

$$E(W_{AA}) = M_{AA} + 2E(W_A^{\text{out}}) \tag{47}$$

and similarly

$$E(W_{BB}) = M_{BB} + 2E(W_B^{\text{out}}) \tag{48}$$

$$E(W_{CC}) = M_{CC} + 2E(W_C^{\text{out}}) \tag{49}$$

Solving (33), (41), (42) and (44)–(49) simultaneously gives:

$$E(W_{AA}) = M_{AA} + 2\left(\frac{M + QM_{AA}}{1 - Q}\right) \tag{50}$$

$$E(W_{BB}) = M_{BB} + 2q_1\left(M_{AA} + \frac{M + QM_{AA}}{1 - Q}\right) \tag{51}$$

$$E(W_{CC}) = M_{CC} + 2q_2\left(M_{AA} + \frac{M + QM_{AA}}{1 - Q}\right) \tag{52}$$

where $M = M_{BB}p_{AB} + M_{CC}p_{AC}$ and $Q = q_1 p_{AB} + q_2 p_{AC}$.

To find the weight-average molecular weight, we pick a unit of mass at random and compute the expected weight of the molecule of which it is a part (another application of equation 1):

$$\bar{M}_w = \sum_{i=\text{A,B,C}} E(W_{ii})\omega_{ii} \tag{53}$$

where ω_{ii} is the initial weight fraction of monomer ii (i = A, B, C) defined by:

$$\omega_{ii} = \frac{M_{ii}[i]_0}{\sum\limits_{i=\text{A,B,C}} M_{ii}[i]_0} \tag{54}$$

$[i]_0 = A_0, B_0$ and C_0. Substituting equations (50)–(52) into (53) gives:

$$\bar{M}_w = W + 2R + 2G(\omega_{AA} + \omega_{BB}q_1 + \omega_{BB}q_1 + \omega_{CC}q_2) \tag{55}$$

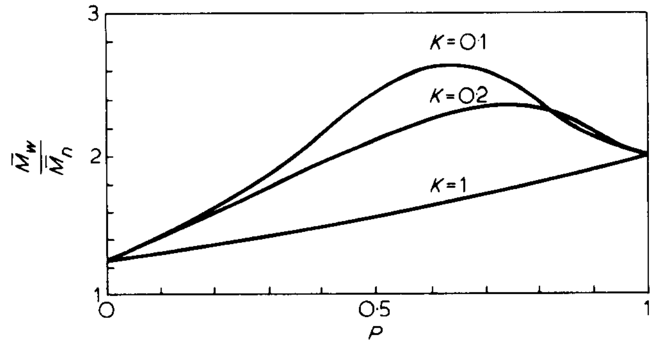


Figure 3 Polydispersity of *MWD* vs. conversion of isocyanate for various degrees of unequal reactivity: $K = k_2/k_1$. $r_1 = 0.5$; $r_2 = 0.5$. $M_A = 1$; $M_B = 1$; $M_C = 0.1$

with

$$W = \sum_{i=A,B,C} \omega_{ii}M_{ii}; R = \sum_{i=B,C} q_1 M_{ii}\omega_{ii}$$

and

$$G = (M + QM_{AA})/(1 - Q)$$

In order ot calculate number-average molecular weight we need to combine the above calculated expected weights in a different way, as discussed earlier. We now want to pick polymer molecules equally by *number,* not as above which, as discussed, is a *weight*-averaging process. We accomplish this by picking only chain ends, with equal probability. Thus:

$$\bar{M}_n = \sum_{i=A,B,C} E(W_i^{in})x_{ii} \qquad (56)$$

where x_{ii} is the number (mole) fraction of each type of end-group which is *unreacted,* that is, at a chain end:

$$x_{AA} = A_0(1 - p)/\Sigma$$

$$x_{BB} = B_0(1 - q_1)/\Sigma$$

$$x_{CC} = C_0(1 - q_2)/\Sigma \qquad (57)$$

where

$$\Sigma = A_0(1 - p) + B_0(1 - q_1) + C_0(1 - q_2)$$

The final result for number-average molecular weight is:

$$\bar{M}_n = N + R' + G(x_{AA} + x_{BB}q_1 + x_{CC}q_2) \qquad (58)$$

where

$$N = \sum_{i=A,B,C} x_{ii}M_{ii}$$

and

$$R' = \sum_{i=B,C} q_i M_{ii} x_{ii}$$

Equation (58) coincides with the result given by Case which can be derived also by standard mass balance argument. By replacing M_{AA}, M_{BB} and M_{CC} by 1 in equations (55) and (58), we obtain the expressions for $\bar{x}_w$ and $\bar{x}_n$, respectively:

$$\bar{x}_w = 1 + 2R'' + 2G'(\omega_{AA} + \omega_{BB}q_1 + \omega_{CC}q_2) \qquad (59)$$

$$\bar{x}_n = 1 + R''' + G'(x_{AA} + x_{BB}q_1 + x_{CC}q_2) \qquad (60)$$

where

$$R'' = \sum_{i=B,C} q_i\omega_{ii}$$

$$R''' = \sum_{i=B,C} q_i x_{ii}$$

and

$$G' = (p + Q)/(1 - Q)$$

From equations (55) and (58)–(60), it is clear that the terms involving G and G' are the dominant ones as conversion increases. Equally clear is the fact that a polydispersity of 2 is approached asymptotically at high conversion. Study of Case's work[3] reveals the comparative simplicity of the recursive approach.

In *Figure 3* we show some illustrative results demonstrating the effect on polydispersity of unequal reactivity of A for B and C. These results were obtained by employing the kinetic equations of the Appendix with equations (55) and (58); the parameter K is the ratio of rate constants: $K = k_2/k_1$. We see that for equal reactivity $\bar{M}_w/\bar{M}_n$ increases monotonically towards 2 with increasing conversion; in contrast, for unequal reactivity, $\bar{M}_w/\bar{M}_n$ shows a maximum greater than 2 before decreasing to the complete conversion limit of 2. Gandhi and Babu[16] saw similar behaviour in some other unequal reactivity examples.

Average sequence lengths are correspondingly simple to obtain. Referring to *Figure 4*, we define the size or lengths of a BB or CC sequence as the number of times that BB or CC is repeated in the run. Now we pick an A group at random and ask for the expected number of, for instance, BB units $[E(N_{A,BB}^{out})]$ sequentially attached to that A, looking 'out' from its parent molecule:

$$E(N_{A,BB}^{out}) = \begin{cases} 0 \text{ if A has not reacted} \\ E(N_{B,BB}^{in}) \text{ if A has reacted with BB} \\ 0 \text{ if A has reacted with CC} \end{cases}$$

The difference here from calculations of *total* chain lengths is that now another one of the possibilities, reaction with CC, leads to a zero expectation value of the desired quantity. Thus, applying equation (1):

$$E(N_{A,BB}^{out}) = E(N_{B;BB}^{in}) = E(N_{B,BB}^{in})p_{AB} \qquad (61)$$

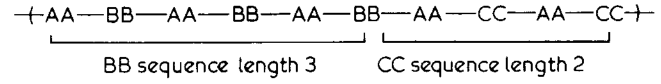


Figure 4 Definition of sequence lengths

Clearly:

$$E(N^{\text{in}}_{\text{B,BB}}) = 1 + E(N^{\text{out}}_{\text{B,BB}}) \tag{62}$$

A second application of equation (1) gives:

$$E(N^{\text{out}}_{\text{B,BB}}) = E(N^{\text{in}}_{\text{B,AA}})q_1 \tag{63}$$

A set of 4 equations in 4 unknowns is completed by recognizing:

$$E(N^{\text{in}}_{\text{B,AA}}) = E(N^{\text{out}}_{\text{B,AA}}) \tag{64}$$

The number- and weight-average sequence lengths are calculated directly from these results since:

$$\bar{N}_{n,\text{BB}} = 1 + E(N^{\text{out}}_{\text{B,BB}}) \tag{65}$$

and

$$\bar{N}_{w,\text{BB}} = 1 + 2E(N^{\text{out}}_{\text{B,BB}}) \tag{66}$$

The geometric quality, which a distribution must possess in order for this approach to work, is clear from these equations. The final results for average sequence lengths of BB and CC are:

$$\bar{N}_{n,\text{BB}} = \frac{1}{1 - r_1 q_1^2}\,; \quad \bar{N}_{n,\text{CC}} = \frac{1}{1 - r_2 q_2^2} \tag{67}$$

$$\bar{N}_{w,\text{BB}} = \frac{1 + r_1 q_1^2}{1 - r_1 q_1^2}\,; \quad \bar{N}_{w,\text{CC}} = \frac{1 + r_2 q_2^2}{1 - r_2 q_2^2} \tag{68}$$

These results agree with Pebbles[13] for the cases which he was able to calculate. The one case for which he obtained an analytical solution was for stoichiometric equivalence at complete conversion where he found $\bar{N}_{n,\text{BB}} = A_0/C_0$ agreeing with equation (67). We need not resort to his arguments to see the breadth of the sequence length distribution. The above calculation again demonstrates the simplicity of the recursive approach. What is missing is a model of conversion vs. time behaviour to give the time evolution of the average values. Discussion of this is given in the Appendix. Unequal reactivity presents no difficulty in this approach. We have dealt with one type of unequal reactivity here, that of differences between B and C groups. The simplicity of the scheme would not be altered, although the volume of simple algebraic equations would increase somewhat, if all groups reacted differently, that is if reactive assymmetry existed within the same difunctional molecule[17]. The case of different reactivity between monomer and polymer groups is also amenable to this approach[18]. In the next case we treat a different sort of step-growth copolymerization.

$A_1B_1A_2B_2$ *step-growth copolymerization*[11]

This case is intended to represent the copolymerization of two different amino- or hydroxy-acids and thus A_1 and A_2 react with B_1 and B_2 but neither A_1 and A_2 nor B_1 and B_2 react with one another. This case turns out to be somewhat more cumbersome mathematically since each monomer now has a 'sense', that is a built-in direction, with a different type of chemical group on each end. The recursive chemical chain is illustrated in *Figure 5*. We now need to define eight probabilities of reaction:

$p_{A_iB_j}$ = probability that A_i reacts with B_j

$p_{B_iA_j}$ = probability that B_i reacts with A_j

$i,j = 1, 2$. Fortunately, due to the nature of the system, we can reduce them to four since:

the number of A_1–B_1 bonds = $A_{10}p_{A_1B_1}$

= the number of B_1–A_1 bonds = $B_{10}p_{B_1A_1}$

leading to:

$$p_{A_1B_1} = p_{B_1A_1} \tag{69}$$

since the initial concentration of A_1 groups, A_{10}, equals the initial concentration of B_1 groups, B_{10}. Similarly:

$$p_{A_2B_2} = p_{B_2A_2} \tag{70}$$

For the cross-reactions we have:

the number of A_1–B_2 bonds = $A_{10}p_{A_1B_2}$

= the number of B_2–A_1 bonds = $B_{20}p_{B_2A_1}$

yielding:

$$p_{A_1B_2} = r p_{B_2A_1} \tag{71}$$

where $r = [A_2B_2]_0/[A_1B_1]_0$ and by similar reasoning:

$$p_{A_2B_2} = \frac{1}{r} p_{B_1A_2} \tag{73}$$

Therefore, we can use the four $p_{A_iB_j}$ and r in the subsequent expressions. These can be related to fractional conversions of A and B groups:

$$p_i = \frac{A_{i0} - A_i}{A_{i0}} \tag{74}$$

$$q_i = \frac{B_{i0} - B_i}{B_{i0}} \tag{75}$$

by simple algebra as follows:

$$p_{A_1B_1} = \frac{B_{10} - B_1}{B_{10} - B_1 + B_{20} - B_2} p_1 = \frac{q_1}{q_1 + rq_2} p_1 \tag{76}$$

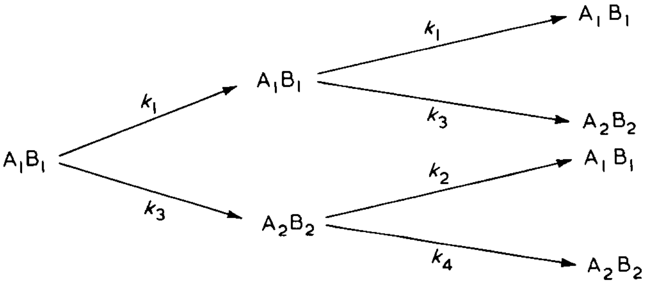


Figure 5 Recursion directions for A_1B_1, A_2B_2

$$p_{\mathrm{A_1B_2}} = \frac{\mathrm{B_{20} - B_2}}{\mathrm{B_{10} - B_1 + B_{20} - B_2}}\, p_1 = \frac{rq_2}{q_1 + rq_2}\, p_1 \tag{77}$$

$$p_{\mathrm{A_2B_1}} = \frac{q_1}{q_1 + rq_2}\, p_2 \tag{78}$$

$$p_{\mathrm{A_2B_2}} = \frac{rq_2}{q_1 + rq_2}\, f_2 \tag{79}$$

In the analysis that follows the weight of the condensation product (e.g. water) will be neglected. This can readily be included, and in fact has been by one of us[18] but as previously demonstrated by Case[3], the effect is negligible and therefore we prefer not to confuse this example more than necessary.

With these preliminaries complete, we now proceed to calculate average molecular weights using the now-familiar recursive approach. We pick an A_i or B_i end-group at random, each in turn, and ask for the expected weight attached to it, looking 'in' and 'out' of its parent molecule. We then proceed along the chain writing simple algebraic equations until recursion occurs, that is, until the set of equations becomes determinate. For this system we obtain:

$$E(W^{\mathrm{in}}_{\mathrm{A_1}}) = M_{\mathrm{A_1B_1}} + E(W^{\mathrm{out}}_{\mathrm{B_1}}) \tag{80}$$

$$E(W^{\mathrm{in}}_{\mathrm{A_2}}) = M_{\mathrm{A_2B_2}} + E(W^{\mathrm{out}}_{\mathrm{B_2}}) \tag{81}$$

$$E(W^{\mathrm{in}}_{\mathrm{B_1}}) = M_{\mathrm{A_1B_1}} + E(W^{\mathrm{out}}_{\mathrm{A_1}}) \tag{82}$$

$$E(W^{\mathrm{in}}_{\mathrm{B_2}}) = M_{\mathrm{A_2B_2}} + E(W^{\mathrm{out}}_{\mathrm{A_2}}) \tag{83}$$

Applying equation (1):

$$E(W^{\mathrm{out}}_{\mathrm{B_1}}) = E(W^{\mathrm{in}}_{\mathrm{A_1}})p_{\mathrm{A_1B_1}} + E(W^{\mathrm{in}}_{\mathrm{A_2}})rp_{\mathrm{A_2B_1}} \tag{84}$$

$$E(W^{\mathrm{out}}_{\mathrm{B_2}}) = E(W^{\mathrm{in}}_{\mathrm{A_1}})\frac{1}{r}p_{\mathrm{A_1B_2}} + E(W^{\mathrm{in}}_{\mathrm{A_2}})p_{\mathrm{A_2B_2}} \tag{85}$$

$$E(W^{\mathrm{out}}_{\mathrm{A_1}}) = E(W^{\mathrm{in}}_{\mathrm{B_1}})p_{\mathrm{A_1B_1}} + E(W^{\mathrm{in}}_{\mathrm{B_2}})p_{\mathrm{A_1B_2}} \tag{86}$$

$$E(W^{\mathrm{out}}_{\mathrm{A_2}}) = E(W^{\mathrm{in}}_{\mathrm{B_1}})p_{\mathrm{A_2B_1}} + E(W^{\mathrm{in}}_{\mathrm{B_2}})p_{\mathrm{A_2B_2}} \tag{87}$$

The weight-average molecular weight is, as before, the expected weight of a molecule to which a randomly chosen monomer unit belongs. This must be an average weight, the expected weights attached to each type of monomer by the respective monomer weight fraction. Thus, analogously to equation (53):

$$\bar{M}_w = \sum_{i=1,2} \omega_i E(W_i) \tag{88a}$$

or

$$\bar{M}_w = \omega_1 E(W_1) + (1 - \omega_1)E(W_2) \tag{88b}$$

where

$$E(W_1) = E(W^{\mathrm{in}}_{\mathrm{A_1}}) + E(W^{\mathrm{out}}_{\mathrm{A_1}}) = E(W^{\mathrm{in}}_{\mathrm{B_1}}) + E(W^{\mathrm{out}}_{\mathrm{B_1}})$$

$$E(W_2) = E(W^{\mathrm{in}}_{\mathrm{A_2}}) + E(W^{\mathrm{out}}_{\mathrm{A_2}}) = E(W^{\mathrm{in}}_{\mathrm{B_2}}) + E(W^{\mathrm{out}}_{\mathrm{B_2}})$$

and

$$\omega_1 = \frac{M_{\mathrm{A_1A_{10}}}}{M_{\mathrm{A_1B_1A_{10}}} + M_{\mathrm{A_2B_2A_{20}}}} \tag{89}$$

Solving (80)–(87) and substituting into equation (88) gives:

$$\begin{aligned}\bar{M}_w = {} & \frac{1}{(1 - p_{\mathrm{A_1B_1}})(1 - p_{\mathrm{A_2B_2}}) - p_{\mathrm{A_1B_2}}p_{\mathrm{A_2B_1}}} \times \\ & \{\omega_1(M_{\mathrm{A_1B_1}}[(1 - p_{\mathrm{A_2B_2}}) \times (1 + p_{\mathrm{A_1B_1}}) + p_{\mathrm{A_1B_2}}p_{\mathrm{A_2B_1}}] \\ & + M_{\mathrm{A_2B_2}}[rp_{\mathrm{A_2B_1}} + p_{\mathrm{A_1B_2}}]) + \\ & (1 - \omega_1)(M_{\mathrm{A_2B_2}}[(1 - p_{\mathrm{A_1B_1}})(1 + p_{\mathrm{A_2B_2}}) + \\ & p_{\mathrm{A_1B_2}}p_{\mathrm{A_2B_1}}] + M_{\mathrm{A_1B_1}}[\frac{1}{r}p_{\mathrm{A_1B_2}} + p_{\mathrm{A_2B_1}}])\}\end{aligned} \tag{90}$$

By previous arguments, the number-average molecular weight is given by:

$$\bar{M}_n = \sum_{i=1,2} x_i E(W^{\mathrm{in}}_i) \tag{91a}$$

or

$$\bar{M}_n = x_1 E(W^{\mathrm{in}}_{\mathrm{A_1}}) + (1 - x_1)E(W^{\mathrm{in}}_{\mathrm{A_2}}) \tag{92b}$$

where x_1 is the mole fraction of unreacted type 1 end-groups:

$$x_1 = \frac{\mathrm{A_{10}}(1 - p_{\mathrm{A_1B_1}} - p_{\mathrm{A_1B_2}})}{\mathrm{A_{10}}(1 - p_{\mathrm{A_1B_1}} - p_{\mathrm{A_1B_2}}) + \mathrm{A_{20}}(1 - p_{\mathrm{A_2B_1}} - p_{\mathrm{A_2B_2}})} \tag{93}$$

The result for $\bar{M}_n$ is:

$$\begin{aligned}\bar{M}_n = {} & \frac{1}{\left(\frac{1}{r}\right)(1 - p_{\mathrm{A_1B_1}} - p_{\mathrm{A_1B_2}}) + (1 - p_{\mathrm{A_2B_2}} - p_{\mathrm{A_2B_1}})} \times \\ & (1 - p_{\mathrm{A_1}}) \left\{ \frac{(1 - p_{\mathrm{A_1B_1}} - p_{\mathrm{A_1B_2}})[M_{\mathrm{A_2B_2}}p_{\mathrm{A_2B_1}} + \left(\frac{1}{r}\right)M_{\mathrm{A_1B_1}}(1 - p_{\mathrm{A_2B_2}})]}{(1 - p_{\mathrm{A_1B_1}})(1 - p_{\mathrm{A_2B_2}}) - p_{\mathrm{A_1B_2}}p_{\mathrm{A_2B_1}}} + \frac{(1 - p_{\mathrm{A_2B_2}} - p_{\mathrm{A_2B_1}})\,[\left(\frac{1}{r}\right)M_{\mathrm{A_1B_1}}p_{\mathrm{A_1B_2}} + M_{\mathrm{A_2B_2}}(1 - p_{\mathrm{A_1B_1}})]}{(1 - p_{\mathrm{A_1B_1}})(1 - p_{\mathrm{A_2B_2}}) - p_{\mathrm{A_1B_2}}p_{\mathrm{A_2B_1}}} \right\}\end{aligned} \tag{94}$$

Mass balance considerations lead to the simpler expression:

$$\bar{M}_n = \frac{M_{A_1B_1} + rM_{A_2B_2}}{(1 - p_{A_1B_1} - p_{A_1B_2}) + r(1 - p_{A_2B_1} - p_{A_2B_2})} \quad (95)$$

Case[3] obtained equation (95) although he was unable to determine the weight-average molecular weight. Expressions for weight- and number-average degrees of polymerization are obtained simply by changing $M_{A_1B_2}$ and $M_{A_2B_2}$ to 1 in the corresponding expression for the average molecular weight. As noted earlier, Peller[11] has obtained results for this case (for $\bar{x}_w$ and $\bar{x}_n$ only) in terms of 'sequential' probabilities rather than the Markov chain transition probabilities, $p_{A_iB_j}$. However, the two sets of probabilities are related algebraically and the $\bar{x}_w$ and $\bar{x}_n$ versions of equations (90) and (94) give results identical to those of Peller[11].

Average sequence lengths of type 1 or type 2 monomers are obtained straightforwardly by the recursive approach for this case. Following the methods of the previous sections we find very simply:

$$\bar{N}_{n,A_1B_1} = \frac{1}{1 - p_{A_1B_1}}; \quad \bar{N}_{n,A_2B_2} = \frac{1}{1 - p_{A_2B_2}} \quad (96)$$

$$\bar{N}_{w,A_1B_1} = \frac{1 + p_{A_1B_1}}{1 - p_{A_1B_1}}; \quad \bar{N}_{w,A_2B_2} = \frac{1 + p_{A_2B_2}}{1 - p_{A_2B_2}} \quad (97)$$

Note again the geometrical quality of the distributions which a polymerization scheme must yield if it conforms to the assumptions inherent in this recursive approach. The above results are buried within those of Peller[11] and are a much simpler means to the results of Sorta and Melis[14] on sequence distributions in finite length copolycondensation.

DISCUSSION AND CONCLUSIONS

We have described a technique for obtaining average values of molecular weight, chain length and sequence distributions in linear copolymerization. The technique is extremely simple to use, even for complex multicomponent copolymerizations. It has the added conceptual benefit of exposing and exploiting the recursive nature of the first order Markov chain process. While the emphasis in this presentation was on demonstration of the technique, some new results were also obtained, particularly in the AA, BB, CC case for $\bar{M}_w$, and the average sequence lengths. These are especially useful in the study of segmented urethane polymerization.

Clearly the technique has much greater generality for study of multicomponent linear and nonlinear copolymerization.

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APPENDIX

Predicting time-dependent behaviour

Until now we have effectively ignored the time evolution of the distribution by burying it in the extents of reaction. We here comment briefly on the kinetic equations necessary to predict the time-dependent behaviour. We will do this by writing the mass balance relations and taking advantage of certain stoichiometric facts. The illustration given here is for the AA, BB, CC system. Application to the A, B, A_2B_2 system will be straightforward.

There are two reactions occurring:

$$A + B \xrightarrow{k_1} AB \quad (A1)$$

$$A + C \xrightarrow{k_2} AC \quad (A2)$$

Writing the batch reactor mass balances gives (assuming first order reactions in all species):

$$-\frac{dA}{dt} = k_1 AB + k_2 AC \quad (A3)$$

$$-\frac{dB}{dt} = k_1 AB \quad (A4)$$

$$-\frac{dC}{dt} = k_2 AC \quad (A5)$$

Only two of the above three equations are independent since:

$$A_0 - A = B_0 - B + C_0 - C \quad (A6)$$

In terms of the extents of reaction equations (A3)–(A6) become:

$$\frac{dp}{dt} = [k_1 B_0(1 - q_1) + k_2 C_0(1 - q_2)](1 - p) \quad (A7)$$

$$\frac{dq_1}{dt} = k_1 A_0(1 - q_1)(1 - p) \quad (A8)$$

$$\frac{dq_2}{dt} = k_2 A_0(1 - q_2)(1 - p) \quad (A9)$$

$$p = q_1 r_1 + q_2 r_2 \qquad \text{(A10)}$$

This system is readily integrated numerically to obtain $p(t)$, $q_1(t)$ and $q_2(t)$ and thus average properties varying with time. For equal reactivity, $k_1 = k_2 = k$, this system admits a simple analytical solution:

$$p(t) = \frac{kA_0 t}{kA_0 t + 1}\ ; \quad q_1(t) = q_2(t) = \frac{1}{r}\, p(t) \qquad \text{(A11)}$$

$r = r_1 + r_2$. As shown previously, all the reaction probabilities used in the earlier calculation can be calculated from the knowledge of a single conversion (p, q_1 or q_2) for this case.

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